

Abstract No. Lin0245

Surface vs. Bulk Structure, Composition, and De-protection in Ultra-thin Chemically Amplified Photoresists

J. Lenhart, S. Sambasivan, E. Lin, R. Jones, C. Soles, W. Wu, D. Fischer (NIST), D. Goldfarb, M. Angelopoulos (IBM)

Beamline(s): U7A

Introduction: Chemically amplified photoresists are extremely prone to interfacial or surface phenomenon. Striking examples include T-topping, footing, and undercutting. If an interfacial excess or depletion of the photogenerated acid, either from atmospheric contamination, evaporation, or segregation within the film is present, differences between the bulk and the interfacial resist structure, composition, and de-protection kinetics will occur. This becomes increasingly important with the drive towards sub-100 nm lithography. As the resist film thickness continuously decreases, interfacial regions dominate the film behavior and it becomes crucial to understand both their physical and chemical nature. To this end, we use Near Edge X-ray Absorption for Fine Structure (NEXAFS) measurements to simultaneously compare differences between the surface (top 2 nm to 5 nm) and bulk (up to 100 nm) of a lithographic film in terms of the de-protection reaction and chemical composition. NEXAFS measurements were also used to understand how the surface chemistry of both organic and inorganic anti-reflective coatings / hard masks and trace atmospheric contaminants can affect resist performance.

Methods and Materials: We demonstrate these capabilities on a system consisting of a photoacid generator (PAG), bis(p-tert-butylphenyl) iodonium perfluorooctanesulfonate (PFOS), in model photoresists, poly(hydroxystyrene) (PHS) and its protected analog, poly(t-butoxycarboxystyrene) (PBOCSt). Specifically, we simultaneously compare differences in the bulk and surface chemical composition as a function of PAG concentration and processing conditions (post-apply bake, PAB; exposure; and post-exposure bake, PEB). This unique data provide valuable insight into the mechanism of line profile deviations or changes in the de-protection chemistry at resist interfaces.

Results: NEXAFS data showed that model resist films exhibited significant surface segregation of the photoacid generator (PAG) at the air interface. The PAG surface mole fraction was (20 to 70) times greater than the bulk mole fraction and the amount of surface segregation was dependent on the polarity of the polymer. NEXAFS also revealed that the PAG surface fraction was reduced after a post exposure bake. In the absence of delay times between processing steps, the PAG surface enhancement led to a faster deprotection reaction rate near the air interface relative to the bulk. However, when significant post exposure delay times were incorporated into the processing, NEXAFS showed that the surface deprotection reaction was incomplete after post exposure baking. Comparison of carbon K-edge, and oxygen K-edge spectra showed that the incomplete surface reaction was very localized at the air interface, only extending (1 to 6) nm from the surface.

Acknowledgments: This work was generously supported by the Defense Advanced Research Projects Agency Advanced Lithography program under contract N66001-00-C-8803.

References: J. L. Lenhart, E. K. Lin, C. L. Soles, R. L. Jones, W. L. Wu, D. A. Fischer, S. Sambisivan, D. L. Goldfarb, and M. Angelopoulos, "Probing Surface and Bulk Deprotection in Resist Films using NEXAFS", Proc. ACS Div. Poly. Mat.: Sci. and Eng., **87**, 417, Boston, MA, 2002.